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Magnesium.

AN important feature of the progress of metallurgy during the last twelve months has been the exceptional interest taken in magnesium alloys. Conferences and discussions have been organised, and a large amount of research has reached the stage of practical development, with the result that there has been a considerable increase in the number of scientific books and papers devoted to the subject, while manufacturers in all countries where a magnesium industry has become established have issued brochures of a high standard of excellence, describing the properties and uses of their products. Although, for economic reasons, much of this activity has been centred in Germany, other countries have shared in the movement. The discussion held at the London Congress of the International Association for Testing Materials and the appearance of Haughton and Prytherch's monograph on "Magnesium and its Alloys," are noteworthy contributions to the subject; but the events which probably attracted most attention were the German conferences on magnesium, the first at Berlin on November 5th and 6th, 1937, and the second at Frankfurt on January 12th, 1938. These conferences were made the occasion of a large number of references in technical journals to recent developments in the production and uses of the metal and its alloys. One of the most valuable of these articles was by K. Bungardt,[1] who reviewed the progress made in Germany and elsewhere in the production of magnesium and in the melting, casting, heat treatment, and protection of magnesium alloys. This is a well-documented statement of the position, with eighty-five references. The proceedings of the conferences were well reported at the time,[2] and a selection of the papers presented has since been published[3] under the title "Werkstoff Magnesium." These papers deal with the physical and mechanical properties of magnesium and its alloys, sand and chill castings, die castings, working, machining, corrosion and surface protection, industrial applications, importance as materials of construction, and principles of design. No fresh information became available about the physical constants of magnesium metal, and the data recorded cannot so easily be critically assessed as those set out in the Metals Handbook, 1936, but one useful addition is derived from two papers published concurrently. The density of liquid magnesium over the range 675 to 850 deg. Cent. was found by H. Grothe and C. Mangelsdorff[4] to be a linear function of the temperature, viz., $1{\cdot}584 - 0{\cdot}00018\ (t - 675)$. This gives a density of 1·5885 for the liquid at the melting point. E. Pelzel and F. Sauerwald[5] found a specific volume at the melting point (650 deg. Cent.) of 0·631 in the liquid condition and 0·606 in the solid, the corresponding densities being 1·585 and 1·649. This corresponds to a volume contraction on solidification of about 4 per cent. Since the specific volume of magnesium at room temperature is 0·573, the solid contraction is 5·5 per cent. of the volume of the solid at the melting point, and the total linear contraction is therefore 1·82 per cent. of the length at 650 deg. Cent. Pelzel and Sauerwald found that these figures also applied to the aluminium-magnesium alloys. They are of the same order of magnitude as for other metals used in the form of castings, *e.g.*, the freezing contraction is similar to that of iron and the solid contraction somewhat less.

At about the same time as the Berlin conference, tentative specifications for German standard magnesium alloys were published.[6] Details of compositions and tests are reproduced in the table on the following page. They indicate that aluminium is still regarded as the most important alloying element, and as an essential constituent when high strength is required. Of the other elements, manganese and zinc are those most frequently used. The list of tentative standards naturally contains the well-established alloys and does not refer to the latest developments of the last few years, though these are described in Bungardt's paper and other communications in the journals referred to. Several of the developments to which attention is drawn originated in the work of the National Physical Laboratory. For example, reference is made (*a*) to the alloys of magnesium with aluminium and cadmium, which are notable for their relatively good ductility (12 to 14 per cent. elongation with tensile strengths of 25 to 22 tons per square inch); (*b*) the age hardening alloys containing 8 per cent. of aluminium and 2·5 per cent. of silver, which after heating at 410 deg. Cent., followed by precipitation hardening at 175 deg. Cent. for two or three days, gave a tensile strength of 27 tons per square inch, with nearly 5 per cent. elongation; and (*c*) the alloys showing improved strength at temperatures up to 300 deg. Cent., such as the alloy with 10 per cent. of cerium and 1·5 per cent. of each of the metals cobalt and manganese—an alloy which is without ductility at room temperature, but which has a tensile strength of 7·4 tons per square inch, with 152 per cent. elongation at 300 deg. Cent. The addition of 0·2 per cent. of calcium to the 8 per cent. aluminium alloy reduces its tendency to oxidise, improves its casting properties, and increases its resistance to corrosion by moist atmospheres. The use of protective fluxes in melting and of protective coatings in service cannot, however, be avoided by this means.

A great obstacle to the earlier application of magnesium alloys was their liability to corrosive attack. This has very largely been overcome, so that corrosion is not as serious a difficulty as was at

one time anticipated. Protective coatings are, however, essential, and anodic oxide films and other forms of chemical treatment of the surface are valuable mainly as a basis for paints. Since protective coatings are always subject to local damage, the intrinsic corrodi-

surface appearance, since magnesium hydroxide can be formed in moist air and dissolved in rain water without any apparent change in the surface; and tensile tests are more informative than loss of weight, since instances have occurred in which loss of weight

Composition of German Standard Magnesium Alloys, as indicated in First Draft of the Proposed Specification DIN. E 1717.

A. *Wrought Alloys.*

Type.	Approximate composition, per cent.	Condition.	Yield point, kg./mm.²	Ultimate stress, kg./mm.²	Elongation per cent. ($l = 10\,d$).	Brinell hardness No. 5/250/30	Indication of use.
Mg-Al 3 ...	2 to 4 Al 0 to 1·5 Zn 0 to 0·5 Mn Rest Mg	No heat treatment	15 to 18	24 to 29	18 to 8	55 to 60	Easily workable alloy, for forgings with high relief, small stampings, &c.
Mg-Al 6 ...	6 to 7 Al 0 to 1·5 Zn 0 to 0·5 Mn Rest Mg	No heat treatment	18 to 22	27 to 33	16 to 10	60 to 65	Usual alloy for rods, tubes, profiles, and forgings; sheet of limited weldability (short welded joints)
Mg-Al 9 ...	8 to 11 Al 0 to 1·5 Zn 0 to 0·5 Mn Rest Mg	No heat treatment	20 to 28	28 to 37	12 to 6	70 to 80	Highly stressed constructional parts, *e.g.*, engine supports, air screws
		Homogenised	22 to 26	32 to 38	12 to 9	65 to 75	
		Hardened	26 to 30	36 to 43	6 to 2	85 to 95	
Mg-Zn ...	4 to 5 Zn 0 to 0·2 Mn Rest Mg	No heat treatment	16 to 18	24 to 28	18 to 14	50 to 60	Easily workable alloy, stainable in colours, *e.g.*, for office materials
Mg-Mn ...	1 to 2·5 Mn Rest Mg	No heat treatment	8 to 15	18 to 24	8 to 1	40 to 50	Usual alloy for sheet, good corrosion resistance and weldability, *e.g.*, for fuel tanks

B. *Cast Alloys.*

Type.	Approximate composition, per cent.	Condition.		Ultimate stress, kg./mm.²	Elongation per cent. ($l = 10\,d$).	Brinell hardness No. 5/250/30	Indication of use.
G Mg-Al ...	7 to 11 Al 0 to 0·5 Zn 0 to 0·5 Mn Rest Mg	Sand cast	No heat treatment	16 to 20	3 to 6	50 to 60	Continuously stressed parts, *e.g.*, aircraft engine case
			Homogenised	23 to 29	5 to 12	55 to 65	For high ductility
			Hardened	24 to 29	1 to 5	70 to 90	For high yield and hardness
		Chill cast	No heat treatment	16 to 24	2 to 8	55 to 65	Chill castings of all kinds
G Mg-Al 3-Zn	2·5 to 3·5 Al 0·5 to 1·5 Zn 0 to 0·5 Mn Rest Mg	Sand cast; no heat treatment		14 to 17	7 to 10	40 to 50	Liquid-tight castings, *e.g.*, for oil pressure transmission
G Mg-Al 4-Zn	3 to 4·5 Al 2 to 3·5 Zn 0 to 0·5 Mn Rest Mg	Sand cast; no heat treatment		17 to 22	5 to 9	45 to 55	Substantial parts, *e.g.*, aircraft landing wheels
G Mg-Al 6-Zn	5 to 6·5 Al 2 to 3·5 Zn 0 to 0·5 Mn Rest Mg	Sand cast; no heat treatment		16 to 20	3 to 6	50 to 60	Continuously stressed parts, *e.g.*, engine supports; usual alloy for castings used in electro-technology, precision and optical work, machine tool construction
G Mg-Mn ...	1 to 2·5 Mn Rest Mg	Sand cast; no heat treatment		8 to 11	2 to 5	35 to 40	Good corrosion resistance and weldability *e.g.*, for welded fuel and oil tanks
G Mg-Si ...	0·5 to 2 Si Rest Mg	Sand cast; no heat treatment		9 to 13	1 to 4	40 to 45	Liquid-tight castings, *e.g.*, for oil pressure transmission in cases in which the alloy G Mg-Al 3-Zn is not suitable on account of difficulty of casting

bility of the alloys themselves becomes an important problem. Manganese additions have been found to be the most effective in reducing corrosion, possibly owing to the formation of a surface film of manganous hydroxide. In assessing the amount of corrosion, loss of weight may be a more sensitive guide than

was negligible but the ductility of the material had almost disappeared under corroding influences.

At the same time as the composition and methods of protection of the alloys have undergone improvement, the practical difficulties in working and mechanical treatment have largely been overcome by special

attention to rolling temperature, direction of working and rate of deformation. Improved methods of casting and fabrication have made the alloys available in the shapes and sizes required by industry.

The intensive development of the applications of magnesium and its alloys in Germany, though it is certainly being accelerated by the national demand for the avoidance of the use of imported materials, must not be regarded purely as an emergency measure. It is a matter of real technical progress in which all countries should share, and the advances which are now being made will serve in their turn as the foundation of future expansion of the magnesium industry.

References.

[1] *Zeit. Metallkunde*, October, 1937, and elsewhere.
[2] *Metallwirtschaft*, November 5th and 12th, 1937; January 14th, 1938.
[3] By V.D.I. Verlag, Berlin, p. 149. Price in Great Britain 6·05 marks.
[4] *Zeit. Metallkunde*, 1937, 29, 352.
[5] *Metallwirtschaft*, 1937, 16, 1155.
[6] *Zeit. Metallkunde*, October, 1937, 357; *Metallwirtschaft*, November 5th, 1937, 1167.

The Attack of Superheated Steam on Steels.

The modern trend in power station practice towards higher steam temperatures and pressures imposes heavy demands upon boiler materials, both as regards resistance to prolonged stress and capability of resisting destructive oxidation. The creep problem is receiving the greater attention in many laboratories in this country and elsewhere, but considerable progress is also being made in investigating the oxidation of steels by superheated steam, both in work in progress at the National Physical Laboratory for the British Electrical Research Association, and in that undertaken at Purdue University in the United States for the American Society of Mechanical Engineers' Special Research Committee on Critical-Pressure Steam Boilers. The latter investigation, with which this article is mainly concerned, has been described by Potter, Solberg and Hawkins in a recent paper.[1]

These authors draw attention to the facts that in most of the central power stations now under construction in America the steam temperature is to be 480–500 deg. Cent., with a pressure of 1400 lb. per square inch, while at 650 deg. Cent. the reaction between iron and steam is being exploited commercially for the production of large quantities of hydrogen, and, incidentally, of iron oxide. They list twenty-three steels which had been suggested for inclusion in the test programme, but the quantitative work at present carried out is concerned only with six materials, a mild steel, a carbon-molybdenum steel, a silicon-molybdenum steel, and three chromium-molybdenum steels. No tests have yet been carried out on steels of the chromium 18 : 8 nickel type, but considerable insight into their behaviour has been gained from study of the austenitic steels employed in the construction of the high pressure boiler.

This apparatus comprised a water-tube boiler with an evaporating capacity of 50 lb. of water per hour, linked to two superheaters, $\frac{3}{8}$in. and $1\frac{1}{16}$in. internal diameter respectively, in series made from 18 : 8 stabilised by the addition of columbium (niobium). The first superheater was heated by the same gas burner as the boiler, while the second was electrically heated to the desired testing temperature. This second superheater has a core of 1in. diameter 18 : 8 rod, which presumably serves to bring the whole body of steam into the close proximity of the hot wall. The steam piping leads thence to the specimen, which consists of a 3ft. length of 1in. internal, $1\frac{1}{4}$in. external diameter, steel, and is again electrically heated. Three thermo-couples attached to the outside of the specimen and two inserted in the steam pipe on each side of the specimen are brought to the same temperature before a run is commenced. The steam leaving the specimen passes to a condenser and thence to a gas separator where dissolved gas, principally hydrogen, is boiled off from the condensate at a reduced pressure and collected for gas analysis. A similar condenser and gas separator are connected to an alternative line from the second superheater by-passing the specimen, through which about half the steam is diverted.

The boiler is operated on condensate from the steam main of the Laboratory, with addition of caustic soda. Prior to carrying out each test, the specimen is sand blasted to remove scale and to bring the internal surface to a uniform condition, after which it is filled with nitrogen and stored, until assembly in the steam line. When the specimen is placed in position the thermo-couples, heater, and lagging are installed, and the system filled with nitrogen. The temperature is then raised to that required, while the steam generator and secondary superheater are brought to normal operating conditions, steam being discharged through a special starting condenser. After the rate of flow and the temperature of the steam are stabilised, stop valves connecting to the specimen are opened, and those to the starting condenser are closed and the flow through the two branches of the system adjusted by throttle valves near the condensers, which are cooled by the condenser cooling water so that the steam temperature is reduced before the pressure. Thirty minutes after steam first enters the test specimen, collection of gas from the gas separators is commenced.

Potter, Solberg, and Hawkins hoped that they would be able to produce steam sensibly free from hydrogen by means of the stainless steel superheaters, and follow the progress of the oxidation of the steel specimen by observation of the changes in hydrogen content of the issuing steam. In fact, however, the steam by-passed from the superheaters contained hydrogen in surprising proportions, at steam temperatures in excess of 540 deg. Cent., but hydrogen was totally absent below 525 deg. Cent. The gas evolution was found to be unconnected with such factors as the boiler feed pump packing and lubrication, and was proved not to arise from organic matter in the feed water. A section of 25 : 20 chromium nickel steel tubing was then connected in series with the 18 : 8 superheater, and maintained by electrical heating at 500 deg. Cent., and no less than 550 c.c. of gas containing 93 per cent. hydrogen was collected in half an hour. When the temperature was raised to 595 deg. Cent., still more rapid evolution of hydrogen occurred. The authors conclude that these austenitic steels, when used for superheaters at temperatures of 540 deg. Cent. and above, are attacked by steam with the formation of a black layer of oxide which decreases the rate of reaction as the duration of exposure increases. They suggest that any commercial superheater material for "super-high" steam temperature will be subject to a certain amount of oxidation, and that an important factor in the selection of such materials may be the tendency of

the oxide to resist cracking or spalling when subjected to fluctuations of temperature.

The plan to follow the progress of corrosion of the test specimens by the rate of hydrogen evolution was abandoned when it was found that in tests on mild steel, carried out under apparently identical conditions, the total amount of gas collected and its content of hydrogen showed variations of as much as 2 to 1. Moreover, the rate of evolution of gas did not vary with temperature when this fluctuated during a run, and the erratic nature of the observations was not altered by subjecting the specimen to prolonged heating in nitrogen at the test temperature before steam was admitted. These irregularities led to two minor investigations, the results of which are extremely interesting. In the first, five mild steel tubes of the standard size for the steam tests were filled with nitrogen at room temperature and atmospheric pressure, and heated to 540 deg. Cent., the gas given off being collected at atmospheric pressure. The volume of gas given off in four hours varied from 30 c.c. to 200 c.c., and always contained appreciable proportions of carbon dioxide and hydrogen. These results are thought to furnish a possible explanation of the inability to trace steam-metal reaction rates by hydrogen evolution measurements. The second line of inquiry referred to above was to measure the rate of diffusion of hydrogen, through mild steel tubes, ¼in. internal, ⅜in. external diameter and 29in. long, closed at the end by welding. Hydrogen at a gauge pressure of 100 lb. per square inch (usually) surrounded the tube which contained initially either hydrogen or nitrogen at atmospheric pressure. The volume of hydrogen collected at atmospheric pressure from within the tube increased linearly with time and in a more complex way with the temperature. The rate of diffusion was negligible below 315 deg. Cent., but at 540 deg. Cent. 160 c.c. per hour passed through the tube walls under the pressure conditions stated above. When the external hydrogen pressure is decreased the rate of diffusion decreases linearly to zero at zero pressure difference. The authors suggest a parabolic relation between temperature and rate of diffusion; according to most writers on diffusion of hydrogen through steel the relation is exponential.[2] Nitrogen and oxygen did not diffuse in measurable quantities under the conditions of the experiments with hydrogen.

After the setback described above, it was decided to base the results on the weight of oxide that could be removed from the interior of the specimen at the conclusion of each test. This was done by cutting the tube after test into 4in. lengths which were then machined externally until they weighed approximately 100 gm. The pieces were weighed to 0·1 mg. and then immersed for ten to twenty minutes in a solvent maintained below room temperature and containing:

	Parts by weight.
Concentrated hydrochloric acid	100
Antimony trioxide (Sb_2O_3)	2
Stannous chloride ($SnCl_2$)	5

The specimen was washed in alcohol, dried, and reweighed, and the weight of scale computed in terms of grammes per square inch of internal tube surface. Examination of six sections cut from a single test specimen showed that the scale deposit was heavier in the centre of the tube than at the ends as a result of temperature gradient during exposure. The variation could be held within 6 per cent. of the mean for the specimen. Duplicate checks were quite satisfactory; for example, at 595 deg. Cent. and 1200 lb. per square inch the following values were obtained in thirty-six hours:—0·0973 gm., 0·1065 gm., and 0·111 gm. scale per square inch. In a series of tests designed to show the effect of temperature and pressure on the oxidation of mild steel in superheated steam, it was found that the rate of oxidation was markedly affected by temperature, but was independent of pressure. The relationship

$$W = 556 \cdot 10^{-7} \cdot e^{0 \cdot 011 \cdot T}$$

is suggested, where T is the Fahrenheit temperature, as applying up to 595 deg. Cent. The only result available at 650 deg. Cent. is for a test interrupted after twenty-three hours, when 0·297 gm. scale had formed per square inch. An assumption that oxidation in steam follows the square root law obeyed by most cases of oxidation leading to coherent films, suggests a 0·36 gm. coating in thirty-six hours, which is in fair agreement with the exponential relationship suggested by the authors.

An isolated test in which a core of ¾in. round 18:8 steel with a parabolic entrance was mounted in the second half of one of the specimens showed this to increase the scaling from 0·111 g. to 0·171 g. per square inch at 595 deg. Cent. and 1200 lb. per square inch, so that it appears that increased steam velocity adjacent to the surface of the steel accelerates the rate of corrosion at a given temperature. This result, which is reminiscent of Pfeil's experience with the aerial oxidation of iron,[3] is being investigated in more detail by the authors.

Having arrived at the conclusion that pressure is without serious effect on oxidation in steam, Potter, Solberg and Hawkins pass on to more prolonged tests at a lower pressure, namely 175 lb. per square inch, the steam being obtained from the laboratory main, and superheated in an austenitic steel superheater in which alternating current passing through the tube wall supplies the heat. Steam superheated to 595 deg. Cent. was passed through seven tubes in parallel of various steels, each supplied with a gasket and screwed end of 18:8 steel, stabilised with columbium and connected by a nipple of the same steel to a common distribution flange on the hot end of the superheater coil. The discharge ends of the specimens were connected to condensers and gas separators as before. The bundle of seven tubes was electrically heated to the temperature of the steam. After fourteen days at 595 deg. Cent., with a flow rate of 4·8 lb. per hour, the equipment was shut down, 18in. cut from each tube, and the specimens, now 42in. long, reassembled and subjected to a further period of test of seven days' duration. For the first thirty-four hours the temperature was maintained constant at 595 deg. Cent., then ten cycles of temperature were applied, in which the temperature was quickly raised to 620 deg. to 650 deg. Cent., quickly dropped to 230 deg. to 340 deg. Cent., and returned to a steady temperature of 595 deg. Cent. At the end of the test the scale was determined on both sets of pieces as before.

The results of the tests at steady temperature are given in the following table, together with those for the fluctuating treatments.

It will be seen that in these tests the rates of oxidation of all the alloy steels examined appear to be lower than those for mild steel, usually being about two-thirds of the latter. The data also indicate that oxidation proceeds more rapidly during the fluctuating temperature treatment than in the steady tem-

perature stage. The authors, however, point out that these are the results of the very first run with the low-pressure apparatus, and also that they are not confident regarding the efficacy of the inhibitors used in the scale removal when applied to alloy steels. Difficulties were also encountered with chipping of the scale during the machining of some of the materials, *e.g.*, B. & W. Croloy 3 in the first condition, and it is planned in future to make the scale thickness determinations on unmachined portions of the test specimens. When this and some other necessary modifications have been incorporated in the experimental technique, the twenty-two steels referred to above will be compared by means of the low-pressure apparatus. It may be remarked incidentally that the scaling of the mild steel material was only doubled, when the exposure period was increased from 36 to 336 hours in the two series of tests at 595 deg. Cent. and pressures of 1200 and 175 lb. per square inch, so that the decrease in rate of oxidation is actually even more rapid than would accord with the usual parabolic law.

TABLE I.—*Tests in Steam at 595 Deg. Cent. and 175 Lb. Per Square Inch.*

Material.	Chemical composition, per cent.							Weight of scale, gm. per sq. in.	
	C.	Si.	Mn.	S.	P.	Mo.	Cr.	First period.	Second period.
Cold-drawn steel	0·10/0·20	—	0·30/0·60	0·055	0·045	—	—	0·218	0·524
Cold-drawn steel	0·10/0·20	—	0·30/0·60	0·055	0·045	—	—	0·205	0·520
Silicon-molybdenum steel	0·09	1·43	0·15	0·019	0·018	0·50	—	0·140	0·343
Timken/D M	0·11	0·62	0·43	0·013	0·010	0·55	1·75	0·143	0·340
Carbon-molybdenum steel	0·13	0·13	0·48	0·012	0·013	0·51	—	0·162	0·469
B. and W. Croloy 3	0·15	0·45	0·48	0·016	0·011	0·80	3·12	—	0·368
B. and W. Croloy 2	0·104	0·43	0·41	0·011	0·019	0·56	1·99	0·141	0·321

In the investigation at the National Physical Laboratory, the early progress of which was summarised in a paper by Jenkins, Tapsell, Mellor and Johnson to the Chemical Congress of the World Power Conference, 1936,[4] rather closely parallel results have been obtained for low carbon steels. In this investigation steam from a flash boiler operating with de-aerated distilled water is superheated to temperatures up to 650 deg. Cent. at a pressure of 1000 lb. per square inch in an apparatus made of a stainless steel. Series of experiments have been undertaken on specimens free from stress during the exposure period and also on specimens subjected during exposure to stresses which over the prolonged period of test produce deformation. The specimens in the first series of tests consisted of polished cylinders ⅜in. in diameter and 1½in. long, prepared from various carbon and molybdenum steels, the creep properties of which have also been under investigation. These specimens were sectioned and examined microscopically after prolonged exposure to a continuous flow of steam to determine the extent of attack and the nature of the scale. Three photo-micrographs in the Conference paper show the attack on a 0·13 per cent. carbon steel in 100 hours at 600 deg. and 550 deg. Cent., and after 500 hours at 550 deg. Cent. The thickness of scale on these specimens appears to be 0·03 mm., 0·015 mm., and 0·018 mm. respectively. The first value corresponds to 0·09 g. per square inch, a slightly lower figure than that obtained by Potter, Solberg and Hawkins in thirty-six hours at 595 deg. Cent. The other values bear out their suggestion that the scale formed on mild steel in superheated steam is more protective than the average continuous oxide coating. The value, 0·045 gm. per square inch, for 100 hours at 550 deg. Cent., closely agrees with that predictable from the law cited above. It is stated by Jenkins and his co-authors that the rate of oxidation is increased when exposure is intermittent, instead of continuous. Under their conditions of test, increase in steam pressure appears to lead to an increased rate of attack. It is, however, not yet clear whether high pressure steam is more active chemically, or whether the effect is due to changes in the texture of the scale. It is suggested that the changed constitution of iron oxide scale above 570 deg. Cent.—the appearance of the FeO phase—may be a factor in limiting the operation of steam plant. The general conclusion is reached that, under fixed conditions of temperature and pressure, steam attacks at about the same rate all the steels examined, which include carbon and molybdenum types. It will be noted that in the tabulated results of Potter, Solberg, and Hawkins, the carbon-molybdenum steel differed little from the carbon steel in oxidation resistance. Heat treatment prior to testing has not produced any appreciable change in resistance to attack.

The second series of experiments, now in progress, employs an apparatus in which specimens in the form of thin-walled closed tubes are stressed by internal steam pressure. A number of these tests have been completed,[5] but the results have not been published. It seems likely that such tests will reveal, when taken in conjunction with those on stress-free specimens, any tendency for stressing to alter the character or the rate of attack. The limited duration of the tests under normal service stresses in the Purdue University plant might partly obscure such an effect which might yet be developed in service. The two investigations are both in early stages as yet, but the results at present available are in close agreement, and there is every reason to believe that both researches will contribute largely to the development of the power station of the future.

REFERENCES.

[1] Trans. Amer. Soc. Mech. Eng., November, 1937, 59, 725.
[2] See, for example, C. B. Post and W. R. Ham, *Journ. Chem. Physics*, 1937, 5, 913.
[3] *Journ.*, Iron and Steel Inst., 1929 (1), 119, 501.
[4] "Trans." I, 122.
[5] Annual Report, National Physical Laboratory, 1936.

High-Speed Steels Low in Tungsten.

THE problem of the reduction of the amount of alloy elements in high-speed tool steel, and particularly the replacement of tungsten by cheaper and more readily attainable metals, has again been

attracting the attention of German metallurgists. An investigation carried out some years ago by H. Pohl, H. Pollack, and R. Scherer[1] on steels containing chromium, molybdenum, tungsten, and vanadium in the proportions 4 : 8 : 2 : 1 has been extended by R. Scherer,[2] and described by him in a paper on "Experiments with High-speed Steels Containing Little or No Tungsten." These experiments consisted of machining tests (turning and drilling) in which tools made of a wide variety of chromium-molybdenum-tungsten-vanadium steels, sometimes containing cobalt also, were tested to destruction at various speeds of machining, the results being presented in a series of curves in which the life of the tool in minutes is plotted against speed of cutting in metres per minute. As materials for machining, various steels were used with tensile strengths ranging from 46 to 56 tons per square inch, but as these materials varied for each group of tool steel, it is not possible to make a direct comparison of all the experimental compositions used. Under the conditions of the tests, steels with W 10–11, Cr 4, and V 1·2 per cent. were found to give performance equal to that of a standard high-speed steel containing W 18, Cr 4, and V 1 per cent. The tungsten could, without ill-effect, be further reduced to 8 per cent. if 0·8 to 1·0 per cent. of molybdenum were added, and to 6 per cent. if the vanadium were increased to 2·5 per cent. Similar performance was given by a steel with W 2, Mo 8, Cr 4, and V 1 per cent., and by a tungsten-free steel containing Cr 4, Mo 7, and vanadium over 3·5 per cent. Lowering the molybdenum to 3 per cent. with an increase in carbon to 1·5 per cent. and of vanadium to over 4 per cent. in a tungsten-free steel containing 4 per cent. of chromium gave similar results against a 47·5 ton per square inch material, as did a high-speed steel containing C 0·75, W 18, Cr 4, and V 0·5 per cent. Some typical results are given in Table I. The steel which, on the whole, was most

TABLE I.—*Influence of Vanadium on the Life of Tools Made of Molybdenum-Tungsten High-speed Steel, Oil-hardened from* (A) 1220 *deg. Cent.*, (B) 1280 *deg. Cent., and Reheated to* 570 *deg. Cent.*

Steel.	Composition, per cent.				Life of tool in minutes, at cutting speeds of (m. per min.).		
	W.	Cr.	Mo.	V.	20.	19.	18.
A	2	4	8	0·62	5	11	24
	,,	,,	,,	1·17	13	20	36
	,,	,,	,,	2·0	16	19	37
B	6	4	4	1·16	15	28	50
	,,	,,	,,	2·15	20	35	56

Steel A was used on a manganese steel of tensile strength 47 tons per square inch, and steel B on a manganese-silicon steel of tensile strength 52·7 tons per square inch. Cut, 3 mm.; feed, 0·92 mm.

favourably considered was that containing Mo 8, W 2, Cr 4, and V 1, and attempts were made to determine the effect of cobalt on this composition. The results were very irregular, suggesting that the solubility and composition of the carbide formed is affected by cobalt and that the influence of this element will require further study.

The position reached in Germany in connection with recent developments in the production of high-speed steels, low in tungsten, has been summarised by E. Houdremont and H. Schrader.[3] They deal with the effects of varying the proportions of tungsten, molybdenum, and vanadium in the standard high-speed steels containing tungsten, chromium, and vanadium in the proportions 18 : 4 : 1, 20 : 4 : 1·5, or 14 : 4 : 2·5. Houdremont and Schrader are more critical than Scherer of the effect of molybdenum as a substitute for tungsten. They find that all molybdenum-bearing high-speed steels suffer in cutting performance if the conditions of use involve any shock. The deterioration is, however, not serious in comparison with that of the 14 : 4 : 2·5 steel which has proved useful in appropriate circumstances, although it is less tough than the steel of higher tungsten content. In the treatment of the high-speed steels of high molybdenum content a greater tendency to surface decarburisation was observed, and this is a serious matter since surface decarburisation in turn gives rise to a tendency towards hardening cracks. This tendency to decarburisation was also commented on by Scherer, who found that after heating at 1200 deg. Cent. the carbon content of an 8 per cent. molybdenum steel, originally 0·78 per cent., was reduced as follows :—

	Per cent.
At 0·1 to 0·3 mm. below surface	0·16
0·6 to 0·8 mm. ,, ...	0·25
0·9 to 1·0 mm. ,, ...	0·38

At the same time it was shown that no loss of molybdenum occurs. This effect was previously noted by American investigators and special precautions based on the methods of protection evolved in Watertown Arsenal are taken to avoid decarburisation during forging or rolling. These consist of sprinkling the hot ingot or billet with borax in powder form, thus producing a molten protective film which adheres to the steel even in forging. Whatever precautions may be taken, however, long-continued heating causes a "spoiling" of the tool which shows itself in deterioration of cutting performance. The low alloy steels are more susceptible than the high-tungsten steels to overheating, though the actual temperature limit at which burning may begin is lower.

In summing up, Houdremont and Schrader express the opinion that the tungsten content of high-speed steel can without disadvantage be reduced to about 8 per cent. By partial replacement of the tungsten by molybdenum, steels were obtained which were superior in cutting performance to the usual high-tungsten steel. Even by a complete omission of the tungsten and a lowering of the alloy content, molybdenum-chromium-vanadium steels of highly valuable cutting properties can be developed, *e.g.*, one containing C 1·3, Cr 4·3, Mo 3·2, and V 4·7 per cent. Such steels are, however, much less suitable for severe service than the 18 per cent. tungsten high-speed steel.

The authors appear to guard against giving too much support to the idea that molybdenum may completely replace tungsten in high-speed steel. They also indicate that the reduction in cutting efficiency caused by a fall in chromium content cannot be prevented by raising the manganese to 1·5 per cent. It thus appears that whatever changes are made in the proportions of other constituents the chromium content should, for the present, be maintained at 4 to 4·5 per cent.

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[1] *Stahl und Eisen*, 1935, 55, 1001.
[2] *Stahl und Eisen*, 1937, 57, 1355.
[3] *Stahl und Eisen*, 1937, 57, 1317.

Mass Effect in Some Alloy Steels.*

By R. H. GREAVES, D.Sc., and S. H. REES, M.Sc., [Ph.D.

THE importance of alloy steels for constructional purposes is due to the fact that they combine equal or greater ductility (as measured by elongation, reduction of area, notched bar figure, &c.) with greater hardness and strength (elastic limit, yield point, &c.) than carbon steels. The selection of a particular alloy steel for a bar or forging of large dimensions is, however, primarily based, not on the specific mechanical properties of the steel as treated in small sections, but on the action of the alloy elements in enabling the necessary degree of hardening to be achieved at a rate of cooling characteristic of the centre of the forging and determined by its mass, dimensions and thermal constants, and by the conditions of cooling or quenching.

Increase in size can be partly balanced by the use of a quenching medium which gives a more rapid extraction of heat (for example, by the substitution of water quenching for oil quenching), but the properties of large masses can only be substantially improved by utilising an alloy steel in which the transformations on cooling are retarded so that efficient hardening is secured at rates of cooling considerably slower than those required by carbon steels.

The present investigation deals with five steels, a carbon steel containing 0·5–1·0 per cent. nickel, a low nickel-chromium steel, and chromium-vanadium, chromium-molybdenum and manganese-molybdenum steels.

Hardness Tests.—As a preliminary (except in the 0·5–1·0 per cent. nickel steels) test pieces 1in., 2in., and 3in. in diameter and of length equal to their diameter were first annealed at 900 deg. Cent. and afterwards oil-hardened from 840 deg. Cent. They were then sectioned transversely at the middle, one cut face ground and polished, and Vickers diamond hardness tests made on the steel in the hardened condition, and after it had been tempered at temperatures between 200 deg. and 675 deg. Cent. The average hardness figures over the centre inch of each test piece are shown in Fig. 1, which also contains the results of hardness tests made at 1in. from the centre of the pieces, 3¼in., 4½in., and 6in. in diameter, referred to below.

Standard Treatment of Bars.—The following treatments were applied to all the steels investigated except the 0·5–1·0 per cent. nickel steels.

Bars having a diameter of 2in. were annealed at 900 deg. Cent., oil hardened from 840 deg. Cent., and tempered at 500 deg., 550 deg., 600 deg., and 650 deg. Cent. Tempering was followed by cooling in air. The results are given in Table I.

TABLE I.—*Mechanical Properties of Steels Oil Hardened from 840 deg. Cent. and Tempered at Various Temperatures.* Dimensions, 2in. diameter by 5in. length.

Tempering temperature, deg. Cent.	Limit of proportionality	Yield* point.	Maximum load.	Elongation per cent. on 2in.	Reduction of area, per cent.	Yield ratio.	Izod impact value, foot-lb.
	Tons per square inch.						
Ni-Cr (MLW): C 0.42, Ni 1·20, Cr 0·41 per cent.							
500	34	41·0	55·2	21	53	0·74	26
550	33	40·4	54·8	20	51	0·73	26
600	33	41·0	54·5	22	57	0·75	43
650	31	35·4	49·6	23	58	0·71	49
Cr-V (MJC): C 0·43, Cr 1·20, V 0·24 per cent.							
500	56	63·0	73·4	15	46	0·85	17
550	48	55·0	66·6	17	47	0·82	15
600	49	55·0	66·2	18	50	0·83	15
650	44	48·4	58·2	21	56	0·83	37
Cr-Mo (MJB): C 0·34, Cr 1·20, Mo 0·26 per cent.							
500	38	55·0	66·7	16	50	0·82	7
550	37	53·0	65·0	16	49	0·81	13
600	40	54·0	64·8	17	53	0·83	19
650	34	43·2	53·8	20	59	0·80	58
Mn-Mo (LXA): C 0·41, Mn 1·39, Mo 0·32 per cent.							
500	39	59·0	70·2	14	38	0·84	14
550	43	59·0	69·6	16	48	0·84	23
600	40	53·0	64·0	16	42	0·81	20
650	37	49·0	59·1	20	55	0·82	58

* 0·2 per cent. permanent set.

In addition, bars 1in., 2in., and 3in. in diameter, having a length of 5in., and bars 3½in. to 6in. in diameter, having a length at least 50 per cent. greater than the diameter, were annealed at 900 deg. Cent., oil hardened from 840 deg. Cent., and tempered in one batch for two hours at 650 deg. Cent.

0·5–1·0 PER CENT. NICKEL STEEL.

Billets, 3½in. or 4in. square and 12in. long, were oil hardened from 850 deg. Cent., tempered at 600 deg. Cent. for one hour, and cooled in air. An exactly similar treatment was applied to specimens of section 2½in., 1½in., and ¾in. square cut from the same bar. Results of tests are shown in Table II. With the degree of tempering given the maximum load was not affected by the size of section within the limits employed, but the yield ratio showed a considerable decrease when the section treated exceeded 2½in. square and the Izod impact figure fell off at 1½–2½in. square. The rate of cooling had not been sufficient to prevent the formation of pearlite. Ferrite and sorbitic or lamellar pearlite were present in all sizes from ¾in. square upwards (Micro. 1), but the separa-

* Communication from the Research Department, Woolwich.

tion of ferrite was less complete in the small sizes, viz., ¾in. and 1½in. square.

LOW NICKEL-CHROMIUM STEEL.

Bars 2in. in diameter and 5in. long were oil hardened from 840 deg. Cent. and tempered at 500–650 deg. Cent. (Table I). The standard treatment (O.H. 840 deg., T. two hours 650 deg. Cent.) was given to bars from 1in. to 3¾in. diameter (Table III). The separation of pearlite had been suppressed in the 1in. diameter bar, the structure of which after tempering was sorbitic. In the 2in. diameter and larger specimens a considerable amount of ferrite had separated, enclosing grains of sorbitic pearlite (Micro. 2). Hence the considerable fall in properties between 1in. and 2in. diameter, followed by the fairly constant values from 2in. to 3¾in. diameter. This corresponds to the range ¾in. to 2½in. observed in the low-nickel steel

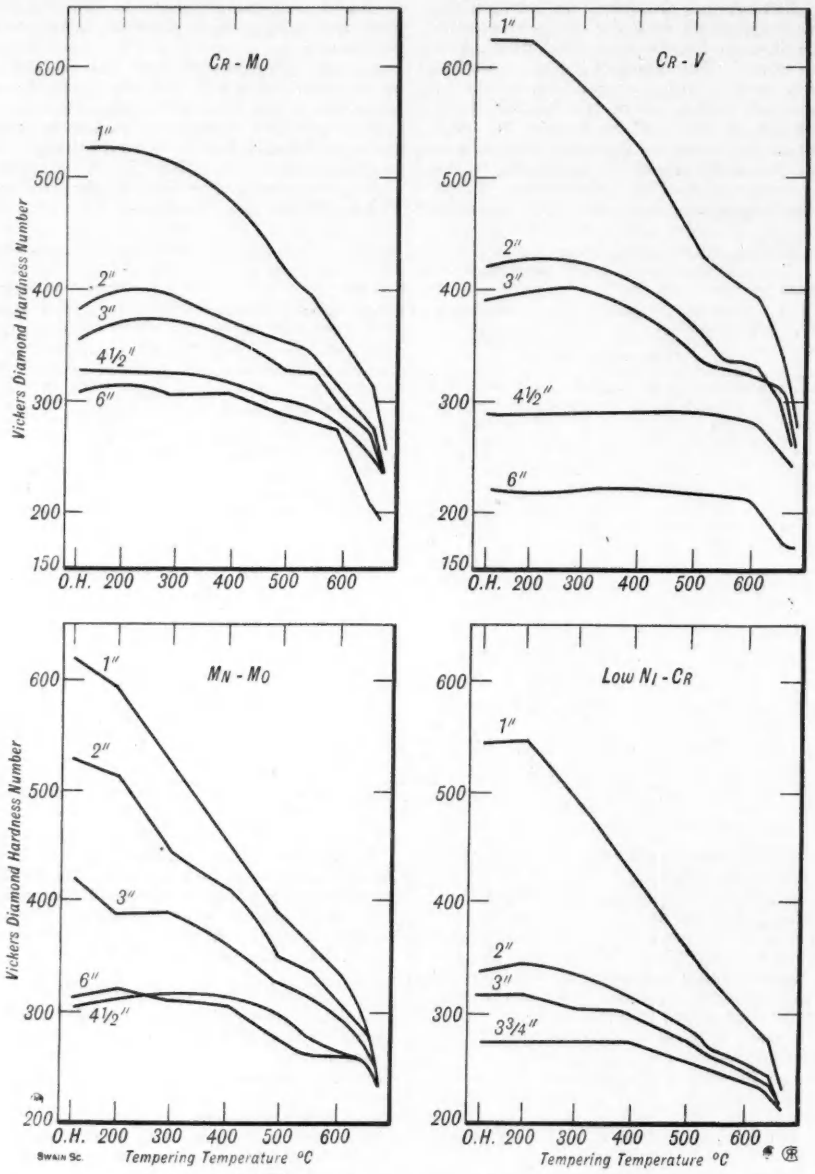


FIG. 1—*Test Pieces 1in., 2in., 3in. Diameter.—Average Hardness Number Over Centre Inch. Test Pieces 3¾in., 4½in., 6in. Diameter.—Hardness 1in. from Centre.*

in which steel the higher values due to more complete hardening were not observed, since they would only occur at a diameter less than ¾in.

CHROMIUM-VANADIUM STEEL.

In addition to the tempering at 500–650 deg. Cent. of 2in. diameter bars oil hardened from 840 deg. Cent. (Table I), the standard treatment (O.H. 840 deg., T. two hours 650 deg. Cent.) was given to bars from 1in. to 6in. in diameter (Table IV). Tempering at 550 deg. and at 600 deg. Cent. gave identical results, confirming the conclusions of Abram and others that the tempering curve of chromium-vanadium steels tends to be nearly horizontal in this range of temperature.

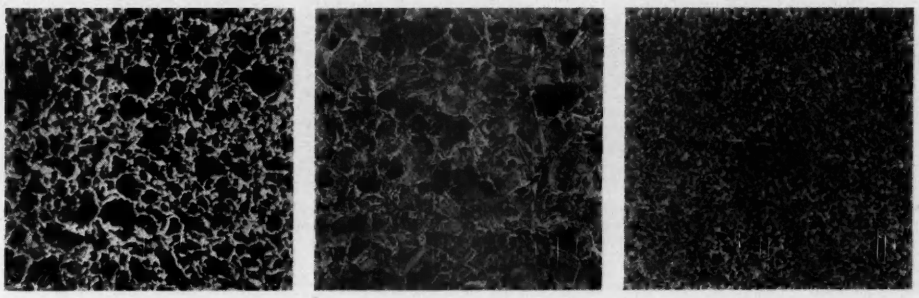
The 1in. and 2in. diameter bars were sorbitic throughout. A considerable separation of ferrite occurs during oil hardening of this steel in bars of diameter 3in. and upwards (Micros. 3 and 4), and the critical rate of cooling which will suppress the formation of pearlite is probably somewhere between the natural rate of cooling in oil of the centre and outside of a 6in. diameter bar (Micros. 7 and 10). Accordingly both the 4½in. and the 6in. diameter bars (unless very fully tempered) show a marked difference in properties on passing from outside to centre. This is shown most clearly in limit of proportionality and yield point, but with the lack of hardening shown by the 6in. diameter bar there is an increase in elongation and impact figure.

Material treated to give a constant maximum load of, say, 55 tons per square inch would probably show a considerable fall in impact value at a diameter of over 3in.

CHROMIUM-MOLYBDENUM STEEL.

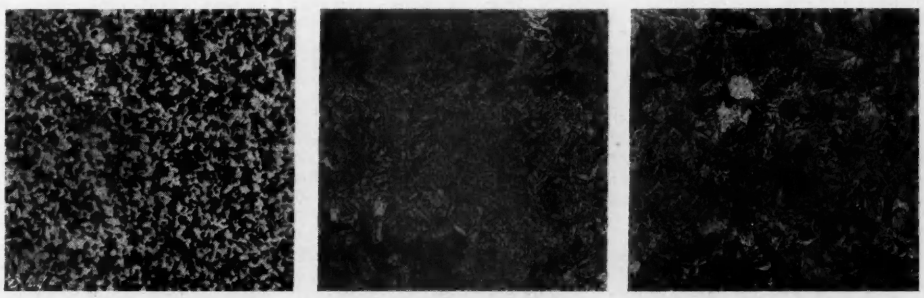
To get a good combination of properties in this steel it was necessary that the tempering temperature should be in the region of at least 650 deg. Cent. After the standard treatment (O.H. 840 deg., T. two hours 650 deg. Cent., Table V) a small decrease in tensile strength was observed with increase in diameter of bars from 1in. to 3in., but from 3in. to 6in. diameter the properties were fairly constant, except for a tendency to show low or variable impact figures in bars of 4½in. and 6in. diameter. The microstructure of the 1in. to 3in. diameter bar consisted of fine sorbite. It became coarser, but showed no appreciable amount of free ferrite in bars of 4½in. diameter (Micro. 5). The structure remained sorbitic throughout the 6in. diameter bar except in the central region, where considerable ferrite separation had occurred (Micros. 8 and 11).

The tests on this steel clearly revealed its advantage over chromium-vanadium steel of similar alloy content. To achieve similar tests in large-diameter bars it was possible to use a lower carbon content and the uniformity of properties in 4½in. and 6in. diameter bar was very much greater than in chromium-vanadium steel.



No. 1. 0·6 per cent. Ni. L M V No. 2. Low Ni-Cr. M L W No. 3. Cr-V. M J C

At Centre of 3½in. Diameter Bar. Magnification 100 Diameters.



No. 4. Cr-V. M J C No. 5. Cr-Mo. M J B No. 6. Mn-Mo. L X A

At Centre of 4½in. Diameter Bar. Magnification 100 Diameters.

TABLE II.—*Mechanical Properties of 0·5–1·0 per cent. Nickel Steels, Oil Hardened from 850 deg. Cent., Tempered at 600 deg. Cent. for One Hour and Cooled in Air.*

	C.	Si.	Mn.	S.	P.	Ni.
LMV	0·46	0·30	0·67	0·036	0·032	0·59
LMW	0·42	0·25	0·72	0·048	0·030	0·86

Mark.	Size of specimen in. sq.	Position of test piece.	Limit of proportionality, tons/in.²	Yield* point, tons/in.²	Maximum load, tons/in.²	Yield ratio.	Elongation per cent. on 2in.	Reduction of area, per cent.	Average Brinell hardness number.	Average Izod impact figure.
LMV	¾	Centre	31	34·2	50·5	0·68	25	61	231	54
	1½	Centre	33	34·0	49·8	0·68	28	59	224	58
	2½	Outside	31	33·0	49·6	0·67	27	59	220	37
	3½	Centre	28	29·4	48·1	0·61	23	51	215	28
	3½	Outside	29	31·0	48·2	0·64	26	55	211	26
LMW	¾	Centre	33	34·4	47·3	0·73	27	62	206	60
	1½	Centre	30	31·0	44·7	0·69	28	59	201	65
	2½	Outside	29	31·0	45·8	0·68	28	62	201	67
	4½	Centre	26	28·0	45·1	0·62	28	55	200	45
	4½	Outside	27	29·0	45·5	0·64	28	56	205	44

* 0·2 per cent. permanent set.

TABLE III.—*Mechanical Properties of Low Nickel-Chromium Steel Oil Hardened from 840 deg. Cent. Tempered Two Hours at 650 deg. Cent. and Cooled in Air. Test Pieces Taken from Centre of Bar.*

	C.	Si.	Mn.	S.	P.	Ni.	Cr.
MLW	0·42	0·23	0·70	0·031	0·030	1·20	0·41

Diameter of specimen, inches.	Limit of proportionality, tons/in.²	Yield* point, tons/in.²	Maximum load, tons/in.²	Yield ratio.	Elongation per cent. on 2in.	Reduction of area, per cent.	Average Brinell hardness number.	Average Izod impact figure.
1	38	45·0	55·2	0·81	23	62	263	70
2	31	35·4	49·6	0·71	23	58	233	49
3	29	34·6	50·2	0·69	23	58	228	35
3¾	28	32·0	48·2	0·66	25	59	218	37

* 0·2 per cent. permanent set.

TABLE IV.—*Mechanical Properties of Chromium-Vanadium Steel Oil Hardened from 840 deg. Cent. Tempered Two Hours at 650 deg. Cent. and Cooled in Air.*

	C.	Si.	Mn.	S.	P.	Ni.	Cr.	V.
MJC	0·43	0·28	0·60	0·038	0·032	0·13	1·20	0·24

Diameter of specimen inches.	Position of test piece.	Limit of proportionality, tons/in.²	Yield* point, tons/in.²	Maximum load, tons/in.²	Yield ratio.	Elongation per cent. on 2in.	Reduction of area, per cent.	Average Brinell hardness number.	Average Izod impact figure.
1	Centre	50	56·4	64·6	0·87	20	54	302	27
2	,,	44	48·4	58·2	0·83	21	56	264	37
3	,,	44	47·0	57·5	0·82	20	56	269	39
4½	,,	31	33·0	52·7	0·63	24	61	233	28
4½	Outside	42	47·0	60·0	0·78	21	55	271	26
6	Centre	24	26·8	46·1	0·58	27	61	207	51
6	1½in. from centre	29	31·0	50·1	0·62	26	61	216	43
6	Outside	40	44·0	56·2	0·78	21	57	264	30

* 0·2 per cent. permanent set.

TABLE V.—*Mechanical Properties of Chromium-Molybdenum Steel, Oil Hardened from 840 deg. Cent. Tempered Two Hours at 650 deg. Cent. and Cooled in Air.*

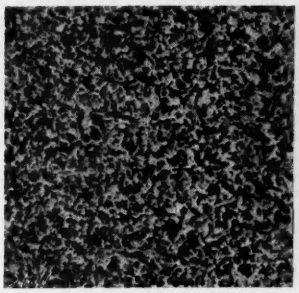
	C.	Si.	Mn.	S.	P.	Ni.	Cr.	Mo.
MJB	0·34	0·18	0·57	0·039	0·039	0·12	1·20	0·26

Diameter of test piece.	Position of test piece.	Limit of proportionality, tons/in.²	Yield* point, tons/in.²	Maximum load, tons/in.²	Yield ratio.	Elongation per cent. on 2in.	Reduction of area, per cent.	Average Brinell hardness number.	Average Izod impact figure.
1	Centre	43	51·2	60·1	0·85	21	63	289	64
2	,,	34	43·2	53·8	0·80	20	59	259	58
3	,,	34	42·0	53·4	0·79	21	58	251	42
4½	,,	33	39·6	50·9	0·78	23	59	234	35
4½	Outside	31	39·2	50·1	0·78	21	59	239	46
6	Centre	30	38·4	50·0	0·77	21	55	228	38
6	1½in. from centre	30	38·4	49·8	0·77	22	58	237	23
6	Outside	34	41·4	53·3	0·77	22	60	250	36

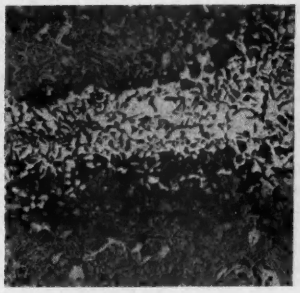
* 0·2 per cent. permanent set.

MANGANESE-MOLYBDENUM STEEL.

Manganese itself has a powerful effect in suppressing the separation of ferrite in quickly cooled steel, and the beneficial influence of molybdenum has endowed the manganese-molybdenum steels with excellent qualities. Good impact figures were not obtained with this carbon content at a maximum load of much above 60 tons per square inch. After the standard treatment (O.H. 840 deg., T. 2 hours, 650 deg. Cent., Table VI) of specimens of different sizes, a slight fall in tensile strength was observed with increase in diameter from 1in. to 3in., though this was less pronounced than in the chromium-molybdenum steel. The impact figure, however, fell in a similar way. From 3in. to 6in. diameter the properties were remarkably constant, and the uniformity of properties from centre to outside was satisfactory. The structures were generally sorbitic. A slight separation of ferrite began to occur at the centre of the 4½in. diameter bar (Micro. 6). The difference in structure between centre and outside, even in the 6in. diameter bar (Micros. 9 and 12), was not sufficient to have any appreciable effect on the properties. The greater hardness at the centre was probably due to some segregation of carbon.



No. 7. Cr-V. M J C



No. 8. Cr-Mo. M J B

No. 9. Mn-Mo. L X A

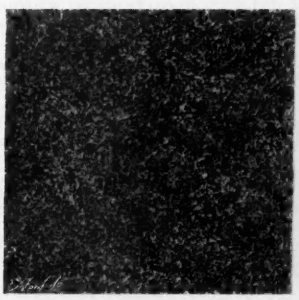
At Centre of 6in. Diameter Bar. Magnification 100 Diameters.

TABLE VI.—*Mechanical Properties of Manganese-Molybdenum Steel, Oil Hardened from 840 deg. Cent. Tempered Two Hours at 650 deg. Cent. and Cooled in Air.*

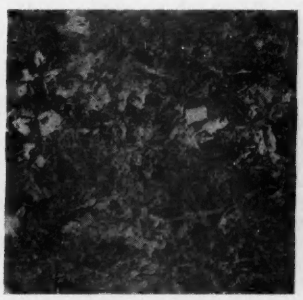
	C.	Si.	Mn.	S.	P.	Ni.	Cr.	Mo.
LXA	0·41 ...	0·22 ...	1·39 ...	0·035 ...	0·030 ...	0·20 ...	0·08 ...	0·32

Diameter of test piece.	Position of test piece.	Limit of proportionality, tons/in.²	Yield* point, tons/in.²	Maximum load, tons/in.²	Yield ratio.	Elongation per cent. on 2in.	Reduction of area, per cent.	Average Brinell hardness number.	Average Izod impact figure.
1	Centre	42	49·6	58·8	0·84	21	58	283	60
2	,,	37	49·0	59·1	0·83	20	55	279	58
3	,,	33	40·4	54·1	0·75	21	55	251	33
4½	,,	31	39·6	53·5	0·74	21	55	253	30
4½	Outside	33	40·0	54·0	0·74	21	56	255	24
6	Centre	32	41·6	55·1	0·75	19	50	254	26
6	1in. from centre	30	37·2	51·5	0·72	21	54	239	23
6	Outside	34	38·2	52·2	0·73	22	56	243	26

* 0·2 per cent. permanent set.



No. 10. Cr-V. M J C



No. 11. Cr-Mo. M J B

No. 12. Mn-Mo. L X A

At Outside of 6in. Diameter Bar. Magnification 100 Diameters

SUMMARY AND CONCLUSIONS.

The effect of mass in the heat treatment of five alloy steels has been investigated. These were a carbon steel containing 0·5–1·0 per cent. of nickel, 1·2 : 0·4 nickel-chromium, 1·2 : 0·24 chromium-vanadium, 1·2 : 0·26 chromium-molybdenum, and 1·4 : 0·32 manganese-molybdenum steels. The low nickel steel in sizes over 2in. square is only toughened by oil quenching; in 4in. square bar its Brinell hardness as oil quenched did not exceed 220. The low nickel-chromium and the chromium-vanadium steels are suitable for 50-ton tensile material in 3in. bar. At this size both yield point and impact figure began to be notably affected by the influence of mass. In chromium-vanadium steel there is a marked difference in properties between the centre and the outside of bars 4½in. in diameter. The beneficial influence of molybdenum in reducing mass effect is demonstrated by the uniformity of properties from centre to circumference in 6in. diameter bars of the steels containing this element.

These results have reference to only a very few of the wide range of compositions now available for meeting ordinary requirements in structural steels, but they illustrate the important principle that overloading a steel with alloy elements which are not strictly necessary for the purpose in view (viz., to obtain certain mechanical properties in a certain size) is undesirable, as the expense involved in the material and in working and treating it does not result in any better combination of properties, but may have the reverse effect.

Hydrogen Attack of Steel.

EARLY experience in high-pressure hydrogenation plant, such as that used for ammonia synthesis under pressures of 100 kilos. to 1000 kilos. per square centimetre at 400 deg. to 600 deg. Cent., and in the hydrogenation of coal at pressures up to 700 kilos. per square centimetre at 450 deg. to 550 deg. Cent., revealed the serious attack on carbon steels under these conditions. The attack consists of decarburisation, associated with cracking, which, even on a microscopic scale, leads to marked deterioration of strength and ductility, and ultimately to failure.

Although certain alloy steels have proved to be far more resistant to hydrogen attack than carbon steels, experimental investigation of the behaviour of carbon steels is still necessary, especially with a view to the elucidation of the mechanism of hydrogen attack. A recent paper by F. K. Naumann on "The Effect of Hydrogen under High Pressure on Carbon Steel" opens with a description and photographs of several examples of failure, due to cracking, of steels exposed to hot hydrogen under pressure, and then goes on to describe experiments carried out to determine the influence of pressure, temperature, and time of exposure on the progress of decarburisation and the related changes in structure and properties. Examination of material which had suffered deterioration under the action of hydrogen was very instructive. A tube exposed on both sides, for two years, to hydrogen at 100 kilos. per square centimetre and 450 deg. Cent. showed decarburisation and numerous flaws, and when drilled under water gave off a considerable volume of gas consisting of 90 per cent. by volume of methane and 10 per cent. of nitrogen. The gas extracted from fine shapings of the same steel contained only nitrogen and hydrogen, indicating that the methane was mechanically held in the cavities. A rod contained in a synthetic ammonia plant in hydrogen under 1000 kilos. per square centimetre at 450 deg. Cent. cracked though under no applied stress. It was almost completely decarburised and the cracking was presumably caused by internal stresses set up by the formation of methane within the steel. Such stresses, even when insufficient to cause fracture, may give rise to considerable alterations in length, and consequent disturbance of smooth working. Another effect of hydrogen attack is the formation of large blisters on the surface of the steel. In one of these blisters the gas was found to consist of 60 per cent. by volume of methane and 40 per cent. of carbon dioxide.

A special apparatus was constructed for the study of the behaviour of steels in the form of tubes, 30 mm. external and 12 mm. internal diameter, into which could be inserted a test piece so arranged that hydrogen had access to it on all sides. It was found that the attack set in under exactly the same conditions, regardless of whether the steel was under stress (as in the tube) or not (as in the inserted test piece). Most of the work was therefore carried out on specimens inserted in tubes, some of which were 80 mm. external and 35 mm. internal diameter. Two carbon steels containing 0·22 and 0·76 per cent. of carbon were first investigated. It was found that loss in weight measurements gave results in good agreement with the depth of decarburisation as determined by microscopical examination of sections. Decarburisation given in the diagrams is calculated depth of decarburisation, *i.e.*, depth calculated on the assumption that there is no wide region of transition between the original and the decarburised structure, an assumption which is never quite correct, but which is approximately true for high experimental temperatures. This method considerably simplified the experimental procedure, and the calculated results have the advantage of representing the average degree of decarburisation better than measurements at one or two positions in the specimen. Micro-examination was, however, always used to supplement the results.

The influence of hydrogen pressure is illustrated in Fig. 1. Decarburisation sets in at a fixed pressure, and the depth of decarburisation increases first quickly and then more slowly. A higher pressure was required to start the decarburisation in the 0·22 per cent. carbon steel than in that with 0·76 per cent., but the presence in the former of more manganese (0·84 per cent.) and chromium (0·14 per cent.) may be significant in this connection.

The influence of duration of exposure to hydrogen is shown in Fig. 2. Decarburisation does not always begin at once. Before the high carbon steel began to decarburise a delay of from ten to twenty hours was found at 500 deg. Cent. and 100 kilos. per square centimetre pressure, and fifty to a hundred hours at 400 deg. Cent. and 300 kilos. per square centimetre pressure.

The influence of temperature is represented in Fig. 3. It was concluded that rate of decarburisation depended on the velocity of the true decarburisation reaction and not on the rate of diffusion of hydrogen. A knowledge of the temperature at which (under given pressure) the attack begins is of importance, but to ascertain the true stability limit very long experimental times would be required.

The progress of hydrogen attack is illustrated by a large number of micrographs. The dendritic axes

of the primary structure were more decarburised than the remainder of the material. At temperatures of 400 deg. or 500 deg. Cent. decarburisation is incomplete and proceeds from the grain boundaries and certain preferred planes into the crystal grains. A strong demarcation of the grain boundaries was recognisable in the region in which decarburisation was not yet visible. In spite of this, large-grained specimens and small-grained specimens showed the simultaneous occurrence of the recrystallisation process rather than the condition of cold work was responsible for the increased decarburisation noted.

The influence of hydrogen attack on the tensile properties and notched bar impact figure was studied in Armco iron and three steels containing 0·11, 0·24, and 0·45 per cent. of carbon. Tensile and notched bar test pieces of the normalised steels were subjected to the attack of hydrogen for 100 hours, except at

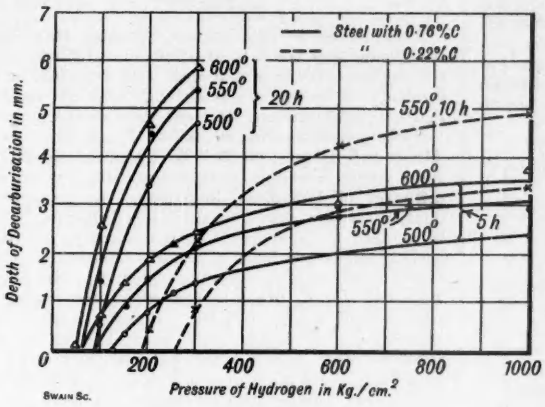


FIG. 1—*Influence of Pressure of Hydrogen on Depth of Decarburisation.*

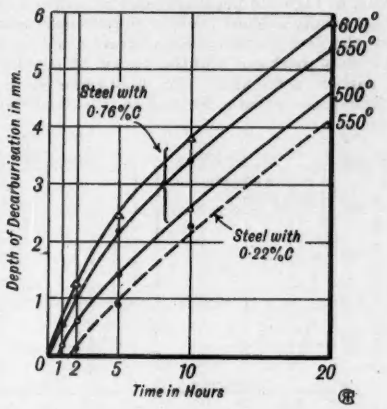


FIG. 2—*Influence of Time on Hydrogen Decarburisation (Pressure 300 Kilos. per Square Centimetre).*

identical amounts of decarburisation as measured by the loss of weight test. This result is in conformity with the now established conclusion that hydrogen shows no preferential diffusion along grain boundaries, though, as already mentioned, Naumann does not consider that diffusion of hydrogen exerts any controlling effect on the process of decarburisation. It was concluded that hydrogen attack was favoured by cold working of the steel. Specimens were compressed 10–50 per cent., then worked to 20 mm. diameter and 20 mm. long, and exposed for five hours to the action of hydrogen at 550 deg. Cent. and 300 kilos. per square centimetre or 600 deg. Cent. and 100 kilos. per square centimetre. There was an increase in the degree of decarburisation up to 40 per cent. compression. In view of the fact that at the temperatures of the experiments, cold-worked steel would undergo rapid recrystallisation, it seems possible that

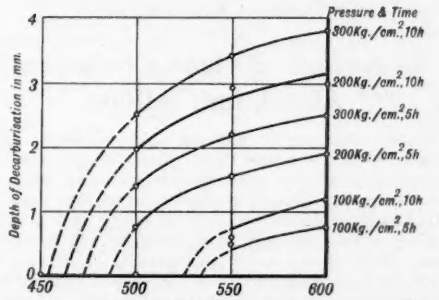


FIG. 3—*Influence of Temperature on Hydrogen Decarburisation.*

600 deg. Cent., when, owing to the rapidity of the attack, ten hours was used. The paper contains details of tests showing deterioration in properties, together with analytical data giving the carbon content of a layer, 1 mm. thick, on the test piece after treatment. The most sensitive indication of hydrogen attack was the notched bar impact figure coupled with a matt grey appearance of the fracture. For example, in the 0·11 per cent. carbon steel after exposure to hydrogen for 100 hours at 100 kilos. per square centimetre pressure and 400 deg. Cent., no loss of carbon could be detected, the yield point, tensile strength, elongation, and reduction of area were not affected by much more than 1 per cent., but the impact figure fell from 27 to 10 mkg. per square centimetre. When the temperature was raised to 450 deg. Cent. there was a very marked fall in strength and almost complete destruction of toughness. In hydrogen at 300 kilos. per square centimetre attack was found to begin at 350 deg. Cent., and the effect of raising the temperature was sufficient to cause a marked deterioration in properties between 350 deg. and 400 deg. Cent. The percentage deterioration of the properties was independent of the carbon content, except that Armco iron maintained its static elongation and reduction of area (but not its impact figure) under rather more severe conditions than the steels. Naumann gives curves, Fig. 4, indicating the limiting conditions of temperature and pressure under which there is no hydrogen attack on steels containing 0·11 and 0·24 per cent. of carbon. These curves are based on tests occupying only 100 hours, but it is stated that 2000-hour tests give limiting temperatures of stability which are 50 to 70 deg. lower. Even allowing for this, the temperature limits regarded as safe by Naumann are much higher than those of N. P. Inglis and W. Andrews,[2] who came to the conclusion that mild steel in the condition normally

found in a large forging can be guaranteed a long life under hydrogen at 250 atmospheres (approximately 250 kilos. per square centimetre) only if the temperature is maintained below about 150 deg. Cent. Naumann definitely regards this limit as unnecessarily low. Specimens tested as tubes under internal pressure were found to be unattacked up to the same temperature and pressure as test pieces inserted in the tubes.

In the theoretical discussion of the process, hydrogen attack at high temperatures and pressures is regarded as essentially different from low-pressure decarburisation, the first process being characterised by the production of methane, and the second by the production of carbon monoxide. In high-pressure hydrogen attack the methane formed in the decarburisation

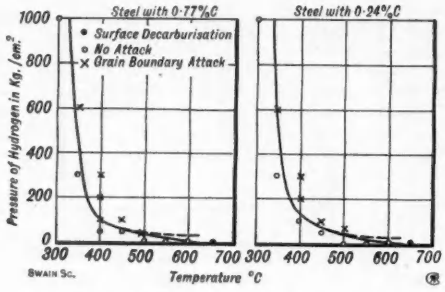


FIG. 4—*Stability Limits for Two Plain Carbon Steels (Duration of Tests 100 Hours).*

accumulates at the place of reaction on account of its slow rate of diffusion, thus giving rise to high stresses which ultimately lead to cracking. Initially, very little carbon is removed, and decarburisation is not detectable by analytical or microscopical methods until some damage to properties has already taken place. With the formation of the first crack the process alters, methane can now escape from the steel, and, on the other hand, hydrogen finds easy access to the interior. This explains the sudden onset of the reaction and the rapid penetration of the decarburisation after a definite time during which the steel appears to be resistant. In contrast with hydrogen attack, low-pressure decarburisation penetrates quite regularly and relatively slowly, leaving behind no trace except for the disappearance of pearlite. The test pieces retain their toughness even when decarburisation penetrates to the middle of the specimen. Moist or unpurified hydrogen will effect this type of decarburisation, but dry pure hydrogen will not. Decarburisation by dry pure hydrogen at atmospheric pressure does not begin below 950 deg. Cent. At 800 deg. Cent. its effect is purely superficial, but in moist hydrogen, oxygen is the principal decarburising agent. Naumann brings forward a considerable amount of evidence for this view, both from published information and from his own experiments. A plate of 0·34 per cent. carbon steel, 5 mm. thick, was welded across a tube of 12 mm. diameter. Into one half unpurified hydrogen at 1 kilo. per square centimetre was introduced, while the other half of the tube was evacuated. The composition of the gases pumped off while the tube was heated at 650 deg. to 900 deg. Cent. by steps of 50 deg. for successive periods of about two hours are given in the following table.

These figures show that the product of decarburisation was carbon monoxide, which first increased in amount, and then fell off again as the steel plate became completely decarburised.

Temperature, deg. Cent.	Volume drawn off, cubic cm. H_2.	CO.
650	1·60	1·34
700	1·76	2·91
750	1·65	3·83
800	2·67	4·27
850	3·72	2·48
900	4·52	0·35

There is some discrepancy between Naumann's conclusion that the rate of diffusion of hydrogen and the carbon content of the steel have no effect on the intensity of hydrogen attack and those of Baukloh and his collaborators. In their most recent paper on "Hydrogen Decarburisation of Pure Iron-Carbon Alloys and Alloyed Steels," W. Baukloh and W. von Kronenfels[3] conclude that below Ac_1 the rate of diffusion of hydrogen determines the progress of decarburisation, and that since the diffusion velocity is reduced by increase in carbon content, the high-carbon steels are least affected. This only applies below Ac_1; at higher temperatures, *e.g.*, 900 deg. or 1000 deg. Cent., other factors affect the result, the high-carbon steels usually suffering most decarburisation. Naumann has worked over a wide pressure range and a somewhat restricted temperature range; Baukloh over a wide temperature range and a very narrow pressure range. A final decision as to the mechanism of hydrogen attack on hot steel is only to be reached by a further linking up of the joint effects of pressure and temperature in initiating hydrogen attack in steels of different composition. Meanwhile, however, the differentiation of hydrogen attack from low-pressure decarburisation emphasised by Naumann is likely to be a useful guiding principle in the interpretation of results.

REFERENCES.

[1] *Stahl und Eisen*, 1937, 57, 889.
[2] *Journal*, Iron and Steel Inst., 1933 (2), 128, 383.
[3] *Archiv für das Eisenhüttenwesen*, 1937–38, 11, 145.

Corrosion of Iron-Chromium-Aluminium Alloys.

IRON-CHROMIUM-ALUMINIUM alloys have been employed on a considerable scale, in the form of electrical resistance wire, for furnaces and electrical heating units. They possess the advantage over the 80 : 20 nickel-chromium alloy that they have a higher specific resistance, and a lower density. At the same time, they have a good resistance to oxidation, but they are more difficult to manufacture and are inferior in mechanical properties. Special attention must be exercised in the provision of suitable supports and in the correct choice of refractories for use with the alloys. In some circumstances they are liable to corrode, and one instance of the corrosion of the iron-chromium-aluminium alloys has been investigated by W. Baumann,* who had noticed that wires which had been in contact with damp asbestos for several hours broke in many places, showing a cavity inside the wire surrounded by rust.

In the investigation suggested by these observa-

* *Metallwirtschaft*, December 3rd, 1937, 16, 1267.

tions he employed four specimens of the wires of different manufacture, including one containing a small amount of cobalt (Table I). For the purpose of testing, the ordinary bend test was discarded as the chance of detecting a spot affected by corrosion was small. In its place the following procedure was

TABLE I.—*Composition of Wires.*

Wire.	Composition, per cent.*			Diameter.
	Cr.	Al.	Co.	mm.
A	25–30	3–5	—	0·50
B	20–25	4–6	2	0·60
C	20–25	3–5	—	0·52
D	20–25	3–5	—	0·68

Finish : A, B, and C oxidised ; D bright.
* Remainder iron.

adopted. Two equal lengths of the wire were polished with emery and degreased, then held at one end in a vice and twisted together from the free end. The length of twisted wire was about 100 mm., and this constituted the specimen which was subjected to corrosion. Assessment of the damage done by the corrosion was made by slowly drawing the wire specimen backwards and forwards over a polished hard wood roller 6 cm. in diameter. In this way the whole length of the wire was subjected to bending, so that no corroded region would escape test ; the bending was sufficiently moderate for the diameter of the wire to have little effect, and a quantitative value could be assigned to the behaviour of the specimen. This value was expressed as the number of breaks in the wire in 100 passes over the roller ; thus a sound wire gave 0/100, *i.e.*, no break in 100 passes. In some cases the length was so reduced by breaks that a smaller total number of passes was all that was possible, so that quotients like 3/100, 2/50, or even 5/1 were obtained, the last value indicating that the wire broke five times before one pass had been completed.

The corrosion tests were made by immersing the wire specimens in separate test tubes filled with a mixture of ground asbestos and distilled water of pasty consistency. After immersion for sixteen hours the specimens were withdrawn and tested in the manner described above. The results are given in Table II. Wire D was unaffected, B and C were

TABLE II.—*After Sixteen Hours in Damp Asbestos.*

Wire.	Ratio (breaks to passes).			Remarks.
	1.	2.	3.	
A	5/1	4/2	6/6	Pronounced rusting
B	3/100	2/100	2/100	Isolated rust spots
C	1/100	3/100	0/100	Slight rusting
D	0/100	0/100	0/100	No attack

slightly attacked and A severely damaged, the aluminium and iron being largely removed, leaving a chromium-rich skeleton of the original wire. Aluminium was found to have gone into solution in the liquid present, the *p*H value of which rose from 5·8 to 8·0 during the sixteen hours. For comparative purposes the effects of wetting the asbestos with 1 per cent. sodium chloride and of 1 per cent. sodium carbonate solutions were investigated (Tables III and IV). In the presence of sodium chloride solution the wire A was again strongly affected, but this time chromium went into solution, and no aluminium was found in the filtrate. The *p*H value increased from 5·8 to 6·8, thus ceasing to rise when the solution became neutral. The alkaline solution caused very little corrosion, probably inducing chemical passivity in the iron. Aluminium, but no iron or chromium, was found in the filtrate. A series of tests carried out with another sample of asbestos of different origin gave different results, none of the wires showing any tendency to fracture. The *p*H value of the filtrate from this asbestos remained practically neutral (6·5 to 7·5) throughout. The main chemical

TABLE III.—*After Sixteen Hours in Asbestos Soaked with 1 per cent. NaCl Solution.*

Wire.	Ratio (breaks to passes).			Remarks.
	1.	2.	3.	
A	1/4	2/6	3/1	Pronounced rust spots with green chromium salts
B	0/100	0/100	0/100	Very slight rusting
C	0/100	1/100	4/100	Isolated rust spots
D	0/100	0/100	0/100	No attack

difference in the two samples of asbestos was the presence of about 1 to 3 per cent. of magnesia in the first, and to this was attributed its greater corrosive action. The chemical attack on aluminium and on iron of a solution of $Mg(OH)_2$ containing 0·186 grammes per litre was demonstrated, while wires A and B showed in this solution the same deterioration

TABLE IV.—*After Sixteen Hours in Asbestos Soaked with 1 per cent. Na_2CO_3 Solution.*

Wire.	Ratio (breaks to passes).			Remarks.
	1.	2.	3.	
A	1/100	0/100	0/100	No rust
B	1/100	0/100	0/100	,,
C	0/100	0/100	1/100	,,
D	0/100	0/100	0/100	,,

as in contact with the first asbestos sample. A 1 per cent. sodium chloride solution without asbestos was found to produce the same effect as with asbestos, but required 1000 hours to do so instead of sixteen (Table V).

This paper illustrates a type of attack that the iron-chromium-aluminium alloys may be subject to, and shows the importance that may attach to small

TABLE V.—*After 1000 Hours in 1 per cent. NaCl Solution.*

Wire.	Ratio (breaks to passes).			Remarks.
	1.	2.	3.	
A	2/50	3/50	1/100	Pronounced rust spots at which the wire broke
B	0/100	0/100	1/100	Marked formation of rust
C	3/100	1/100	2/100	Isolated rust spots near which the wire broke
D	0/100	0/100	0/100	Rusted

differences in the composition of refractories ; but a further expression of opinion on the metallurgical question of why alloy D was immune from attack, and why alloy A with higher chromium content should be worse than alloy C would be welcome. It appears likely to be connected with the presence of oxides or other impurities, which is largely dependent on methods of melting and working the material.

Books and Publications.

The Analysis of Non-ferrous Metals and Alloys. By W. CARTWRIGHT, T. W. COLLIER, and A. CHARLESWORTH. Demy 8vo, pp. vii+296. 1937. London: Charles Griffin and Co., Ltd. 8s.

ANALYTICAL textbooks vary over a wide range from the purely theoretical to the purely descriptive, but books like that under review, which approximate to the last-mentioned class, undoubtedly fulfil a necessary function. The busy industrial chemist does not generally want pages of theoretical discussion, but wants to be told the best and quickest way of attaining the reasonably accurate results that he requires. In many ways this book is an excellent member of its class. Each of the 109 numbered methods arranged in alphabetical order is complete in itself. Where reasons, warnings, or theoretical considerations are necessary they are introduced in the form of brief notes at the end of the method concerned. A heavy responsibility, however, rests with the writer of this sort of textbook. Those using it are compelled merely to follow the directions, and in the absence of critical data are unable to assess the relative merits of alternative processes or to ascertain the amount of the errors inherent in them. On the whole, the methods given in this book appear to have been carefully and painstakingly worked out; whether the accuracy of the results obtainable is always commensurate with the amount of labour involved is perhaps another question. Time-honoured methods are not necessarily the best, and some of the more modern methods are well worth considering on account both of accuracy and speed. This criticism holds good more or less throughout the book. The separations given are largely based on the qualitative table, reprecipitation being relied on to counteract the inevitable co-precipitation. Apart, however, from the fact that reprecipitation is time-consuming, it is not always to be trusted as a means of eliminating the source of error in question. In the absence of figures to prove the contrary one cannot help the suspicion that results obtained by some of these methods may not be as accurate as the obvious care taken in working them out should have warranted. Some, too, by ignoring recent work, cause a quite unnecessary expenditure of time; for instance, antimony in copper (Method 8, page 41) and tin in copper (Method 99, page 226) could both be determined with a very fair degree of accuracy in one-half the time and with the use of one-tenth the weight of sample. Those working with this book should be careful to read the notes connected with any particular process (and to be quite sure that they have found all the notes involved) before starting on it, for these notes contain brief, but sometimes very valuable, information, and they may be appended to a process several pages away. The book ends with four chapters on "Sintered Alloys of Tungsten Carbide and Cobalt," "Babbitts," "Raw Materials," and "Industrial Alloys," respectively, giving schemes for their analysis. There is an appendix, dealing with the use and preservation of platinum apparatus, which seems to be a novel and valuable feature succinctly giving a good deal of information that many chemists have to learn by bitter experience. The authors state that "no attempt has been made to cover the whole non-ferrous field," and it is to be noted that lead alloys are not touched on. The volume is well printed and strongly bound. Only one or two unimportant misprints were noticed. Where time is lacking for trial and investigation (and perhaps, too, the inclination to venture far from beaten paths), this book should prove a good guide to the use of well-tried methods to the best advantage.

The Analytical Chemistry of Tantalum and Niobium. By W. R. SCHOELLER. Demy 8vo, pp. xvi+198. 1937. London: Chapman and Hall, Ltd. Price 21s.

IT must be rare, especially in analytical chemistry, for anyone to write a book based almost entirely on his own work and that of collaborators working with him. The book under review belongs to this very limited category. To those who have to determine tantalum and niobium or to separate them from accompanying elements, Dr. Schoeller needs no introduction; his work is perforce familiar to them. To those who do not have to meddle with these metals and who perhaps regard them merely as evils, and not very necessary ones at that, it may be said, first, that the book deals with many elements besides those mentioned in its title, and second, that it contains a great deal of analytical wisdom gleaned from many years' experience in the separation of elements forming colloidal precipitates. The material of the book is naturally beyond criticism. Dr. Schoeller being so very much on his own ground and the great bulk of the observations recorded being his own (and his colleagues') work, there is not as yet a sufficiently external viewpoint from which to criticise them. Moreover, his very comprehensive results are so coherent, and his experiments so carefully carried out, that it is unlikely that further work will substantially modify his findings. The presentation of this material, is, however, equally admirable; it is a complete account of the subject matter of his thirty-three papers in the *Analyst* viewed as a whole, clearly written and logically arranged. It therefore removes the often very laborious necessity of searching through these papers to make sure one is on the right track. There are, too, a number of general comments not to be found in the papers, comments whose application extends far beyond those substances with which the book deals. Part III contains a dissertation on the use of tannin as a reagent in inorganic analysis comprising separations of a large number of elements, accounts of which would be exceedingly difficult to find elsewhere. The final chapters deal with the qualitative detection of tantalum and niobium and with the literature of earth-acid analysis.

The book marks a new departure inasmuch as it is the first one to be published under the ægis of the Society of Public Analysts and Other Analytical Chemists, and this fact is signalised by a foreword contributed by the Society's President, Dr. G. Roche Lynch. The publishers have made the binding and printing worthy of the outstanding merits of the contents. The printing in especial is excellent, and only one slight printing slip was noticed. The paper is unusually thick, resulting in a presentable volume with easily turned pages. Altogether, this is a book with which all inorganic chemists should make themselves familiar even if their path lies remote from earth-acid analysis.